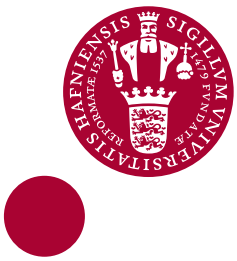

Sorption of chlorinated hydrocarbons from synthetic and natural groundwater by organo-hydrotalcites

Towards their applications as remediation nanoparticles

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Published in:
Chemosphere

DOI:
10.1016/j.chemosphere.2019.124369

Publication date:
2019

Document version
Publisher's PDF, also known as Version of record

Chemosphere 236 (2019) 124369

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Sorption of chlorinated hydrocarbons from synthetic and natural groundwater by organo-hydrotalcites: Towards their applications as remediation nanoparticles

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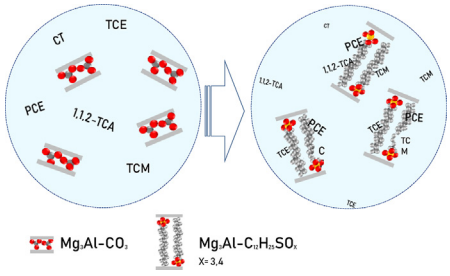
HIGHLIGHTS

- The post-treatment process applied to organo-HT affects its sorption towards CHC.
- Ionic strength and pH have minor effect on the sorption of organo-HT towards CHC.
- Laboratory-calculated K_{om} is used to predict the sorption of CHC in groundwater.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 March 2019
Received in revised form
8 July 2019
Accepted 13 July 2019
Available online 13 July 2019

Handling Editor: Tsair-Fuh

Keywords:
Layered double hydroxide
Contaminated groundwater
Nanomaterials
Sorption isotherms
Organic pollutants
Solvents

ABSTRACT

Chlorinated hydrocarbons (CHCs) are recalcitrant compounds frequently found as contaminants in groundwater. Hydrotalcites (HT) have emerged as promising sorbents due to their tunable properties and anion exchange capacity. Here, two types of organo-HT were synthesized, via coprecipitation, by intercalation of two different anionic surfactants, sodium dodecyl sulfate and sodium 1-dodecane sulfonate. These compounds were first characterized by a suite of techniques to quantify surfactant intercalation and to evaluate their physico-chemical properties. Next, the sorption affinity of these organo-HT towards a suite of CHCs was tested under various conditions, including interlayer surfactant type, single and multiple CHCs systems, and different water chemistry (pH, ionic composition). Sorption coefficients (K_d) and organic-matter-normalized partition coefficient (K_{om}) derived from linear sorption isotherms for individual CHC were inversely correlated to their hydrophobicity in the order of: tetrachloroethylene > tetrachloromethane > trichloroethylene> 1,1,2-trichloroethane > trichloromethane. K_{om} values were further affected by the organo-HT drying process. In contrast, varying water chemistry and pH, and the co-existence of multiple CHCs had little effect on K_{om} values, indicating that competition between CHCs and ionic strength have a marginal effect on the sorption affinity. The inverse linear relationship between CHC hydrophobicity and K_{om} is shown to be a suitable tool to predict organo-HT's

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https://doi.org/10.1016/j.chemosphere.2019.124369

sorption efficiency in complex CHCs contaminated groundwaters. Overall, organo-HT's might be used as potential sorbents for *ex situ* treatment of CHCs in groundwater.

1. Introduction

Chlorinated hydrocarbons (CHCs) account for almost 10% of the contaminants frequently found in soil and groundwater across Europe (van Liedekerke et al., 2014). These hydrophobic organic compounds were used extensively as solvents for metal degreasing, dry-cleaning, pharmaceutical production, pesticides, adhesives, and refrigerants (Huang et al., 2014), leading to numerous events of uncontrolled release into subsurface environments. The properties that have made CHCs attractive for industrial purposes (e.g. stable under aerobic conditions, low flammability, low solubility in water, low viscosity, and higher density than water), make them a real challenge when trying to remove them from the subsurface (Sale et al., 2008). Furthermore, CHCs do not easily biodegrade under natural conditions; thus, they are often found as contaminants of concern (COCs) in soil and groundwater.

For the past few decades, a wide variety of minerals have been used as sorbents for organic pollutants in water (Cornejo and Celis, 2008; Rojas, 2012), including zeolites (Leal et al., 2017), organoclays (Smith and Galan, 1995; Gullick and Weber, 2001), smectites (Lee et al., 2004), and layered double hydroxides (LDH) (Ulibarri and Hermosin, 2001; Bruna et al., 2006; Jobbágy and Regazzoni, 2006; Zaghouane-Boudiaf et al., 2011; Ruan et al., 2013; Zubair et al., 2017). LDH are a family of synthetic and natural inorganic-lamellar hydroxide compounds with a high anionic exchange capacity (calculated around 3 meq/g) (Rives, 2001). LDH have a tunable, brucite-like structure with the general formula: $[M^{II}_{1-x}M^{III}_{x}(OH)_2]A^{n-}_{x/n}.mH_2O$ (Miyata, 1983). Hydrotalcite-like (HT) compounds are a specific group of LDH, composed of positively charged layers of edge-sharing $Mg(OH)_6$ and $Al(OH)_6$ octahedra, that alternate with layers of inorganic anions (e.g. NO_3^-, Cl^-, SO_4^{2-}, CO_3^{-2}) for charge balance, and which also contain water. Organic anions such as aliphatic and aromatic sulfates (You et al., 2002b), carboxylates (Newman and Jones, 1998), or cyclodextrins (Zhao and Vance, 1997) can substitute for the inorganic anions in the HT interlayer (Clearfield et al., 1991), resulting in organo-HT with hydrophobic properties, which increases their sorption affinity towards organic pollutants such as CHCs (e.g., tetrachloroethylene (PCE), trichloroethylene (TCE) and 1,1,1 trichloroethane (1,1,1-TCA) (You et al., 2002a,b; Zhao and Nagy, 2004). Zhao and Nagy (2004) showed that HT (Mg/Al molar ratio = 3:1) with intercalated dodecyl sulfate (DS) forms an effective partitioning medium for trapping CHCs. Similarly, Jobbágy and Regazzoni (2006) determined that solute partitioning was the main sorption mechanism for aromatic compounds by 3:1 HT with intercalated DS and the derived partition coefficients correlated linearly with the solubility (i.e., hydrophobicity) of the aromatic compounds. This linear relationship was also described for CHCs sorption in soils (Chiou et al., 1979; Chiou, 2002), and sorption of herbicides by organo-Mg/Fe LDH (Ruan et al., 2013). The efficiency with which organo-HT can remove CHCs indicates that this process has the potential for application in filters, membranes, or *in situ* permeable reactive barriers to treat groundwater contaminated by CHCs.

CHC sorption by organo-HT has mainly been studied in simple, well controlled laboratory experiments (You et al., 2002a, 2002b; Zhao and Nagy, 2004). These studies provided some key insights into the sorption capacities and mechanisms of organo-HT towards CHCs, however, they have largely ignored the complexity of natural systems, such as varying water chemistry and pH. Moreover, while natural attenuation processes can partly degrade the parent compounds in a spill (e.g. PCE to TCE; tetrachloromethane (CT) to trichloromethane (TCM) (Lawrence, 2006), this often creates a more complex and more toxic dissolved plume in the subsurface. Thus, to assess the applicability of organo-HT for remediation of such complex CHCs plumes, it is necessary to determine how the sorption capacity of organo-HT is affected by varying water chemistry and importantly also by the coexistence of multiple CHCs.

The specific objectives of this study are: (a) to synthesize two types of organo-HT with interlayer DS and dodecane sulfonate (1-DF) and characterize their size, structure, and composition; (b) to determine the sorption affinity and extent of these organo-HT towards individual, common CHCs contaminants (e.g. PCE, TCE, CT, TCM, and 1,1,2-trichloroethane (1,1,2-TCA)); (c) to assess if the sorption coefficient (K_d) of these organo-HT changes in response to varying water chemistry, pH, and the coexistence of multiple CHCs; and (d) to expose organo-HT to a complex contaminated groundwater and compare measured and predicted sorption capacities. Overall, this data will help to identify the optimal organo-HT compound and geochemical conditions for successful removal of CHCs from contaminated groundwater.

2. Materials and methods

2.1. Synthesis of organo-HT

Reagent grade metal nitrates (99.9% of purity), $(Mg(NO_3)_2.6H_2O$ and $Al(NO_3)_3.9H_2O)$, and NaOH were purchased from Sigma Aldrich. Anionic surfactant salts, sodium dodecyl sulfate ($NaC_{12}H_{25}SO_4$) (≥98.5% of purity) and sodium 1-dodecane sulfonate ($NaC_{12}H_{25}SO_3$) (>98.0% of purity) were purchased from Sigma Aldrich and TGI (Japan), respectively. Chemicals were used without further purification. The structures and characteristics of the anionic surfactants are described in Table SM-1. All glassware used in this study was first soaked in 3 M HCl solution overnight, thoroughly rinsed with deionized water (MilliQ, resistivity > 18 Ωcm), and dried at 75 °C before use. All solutions described below were prepared with CO_2-free MilliQ, prepared by overnight sparging with N_2.

Organo-HT with a Mg/Al molar ratio of 3:1 was synthesized by incorporating either DS or 1-DF into the HT via co-precipitation (Clearfield et al., 1991), as illustrated in Figure SM-1 and described below. The synthesis with 1-DF was performed at 40 ± 5 °C to enhance surfactant dissolution, while for DS, it was done at room temperature. For the synthesis, 50 mL of the metal solution (0.75 M $Mg(NO_3)_2.6H_2O$ and 0.25 M Al $(NO_3)_3.9H_2O$) were added dropwise (1–2 mL/min) to a beaker containing 100 mL of surfactant solution (i.e., 0.25 M $NaC_{12}H_{25}SO_4$ or $NaC_{12}H_{25}SO_3$), while keeping the pH constant at 9 by the addition of 1 M NaOH solution with a titrator system (Metrohohm, Tritando 809). Throughout synthesis, the suspension was thoroughly stirred and bubbled with pure N_2 gas to minimize CO_2 influx, i.e., intercalation of carbonate species. At the end of the titration, the slurries were stirred for 1 h at room temperature, then centrifuged, and the supernatant decanted. The wet paste was washed 4–5 times with

deionized water until the supernatant was free of NO_3^- (Mohr salt-H_2SO_4 test). The wet paste was either dried or used directly depending on experiment (Table 1, section 2.4). The dried samples were ground with an agate mortar and pestle and stored in capped-plastic bottles until use. In experiments where the wet paste was used directly, the paste was first weighed and then dispersed into 100 mL of MilliQ and thoroughly stirred. Aliquots of this mixture were then directly added to the sorption experiments. To quantify the concentration of organo-HT in these suspensions, known aliquots were oven dried (75 °C) and then weighed (average of 4 replicates). From here on, we refer to the two synthesized organo-HT as Mg_3Al-DS and Mg_3Al-1-DF, based on the intercalated anion. For comparison, 3:1 HT with interlayer carbonate ($Mg_3Al{-}CO_3$) was also synthesized (details in the Supporting Information, Text S1).

2.2. Characterization of organo-HT

The synthesized organo-HT were analyzed by powder X-ray diffraction (PXRD), infrared spectroscopy (FT-IR), induced couple plasma optical emission spectroscopy (ICP-OES), thermogravimetric analysis (TGA), scanning and transmission electron microscopy (SEM, TEM), laser diffraction, and the Brunner-Emmett-Teller (BET) method, to assess crystal structure, composition, and particle size. Detailed information on organo-HT sample preparation and analysis procedures can be found in the Supporting Information (Text S1).

2.3. Pristine, contaminated, and synthetic groundwater

Four different waters were used in the sorption experiments: MilliQ, synthetic groundwater (SGW), pristine natural groundwater (NGW), and contaminated groundwater (CGW). The last two were collected from a subsurface sedimentary aquifer at an industrial site in Spain, upstream (NGW) and close to an old spill (CGW), respectively. The main CHCs in the CGW were 1,1,2-TCA (55%), 1,1,2-DCA (20%), TCM (8%), and TCE (5%). The NGW and CGW (pH: 7.8 ± 0.2, geochemistry in Table SM-2) were kept refrigerated until use. The SGW (pH: 8.0 ± 0.2) was prepared based on the method described by Smith et al. (2002), and is detailed in the Supporting Information (Text S1).

2.4. Sorption experiments for CHCs

Chlorinated hydrocarbons (CHCs) were purchased from Sigma Aldrich, with purities ≥97% for 1,1,2-TCA and ≥99.0% for CT, TCM, PCE, and TCE. Methanol stock solutions for each CHC and a mixture of TCE, TCM, and 1,1,2 -TCA ($C_0 = 50$ mg/L) were prepared and kept refrigerated until use. Table SM-1 summarizes the main characteristics and abbreviations of CHCs used in this study.

A large set of sorption isotherms (equilibrium concentration (C_e) vs. amount sorbed (q_e)) were determined using batch equilibration at 20 ± 1 °C (Table 1). For this, specific amounts of organo-HT were placed into 20 mL glass vials and spiked with the corresponding CHC stock solution. The vials were fully filled with MilliQ, SGW or NGW (Table 1) to minimize headspace, and then crimp-sealed with Silicone-PTFE septa. The final solid-liquid ratio was 3.2 g/L and the CHC concentrations ranged from 0 to 400 mg/L. Vials were placed upside-down (to minimize volatilization) on a shaker to equilibrate for 24 h. Previous CHC sorption studies with Mg_3Al-DS have shown this to be a sufficient equilibration time (You et al., 2002b; Zhao and Nagy, 2004). The vials were then centrifuged, and 0.5–1 mL of the supernatant were transferred into 20 mL glass vials and crimp-sealed for headspace analysis (section 2.5). Each experiment was performed in duplicate and controls without sorbent were run in parallel.

We first evaluated the effect of interlayer surfactant type on CHC uptake, by determining sorption isotherms for PCE and TCE in MilliQ by Mg_3Al-DS and Mg_3Al-1-DF (both dried at 75 °C following synthesis). The impact of post-synthesis treatment on sorption capacity was determined in experiments with TCE in MilliQ with Mg_3Al-DS (a) dried at 75 °C for 48 h, (b) freeze dried at −76 °C (0.10 mbar, 24 h), and (c) used directly as a wet paste. In a second set of experiments, sorption isotherms were determined for each individual CHC compound by Mg_3Al-DS (added as wet paste) in MilliQ, as well as in ternary solute systems (with equal concentrations of TCE, TCM, and 1,1,2-TCA) to test the effects of different water chemistry (MilliQ, SGW and NGW) and varying pH (6-11) (Table 1). For the pH experiments, the suspension pH was manually adjusted with HCl and NaOH and kept constant for at least an hour, before starting the sorption experiment. The last set of sorption experiments was performed with CGW in a slightly larger set-up, using 100 mL screw-cap vials to which 0.35 g of Mg_3Al-DS was added.

2.5. CHCs analysis and sorption coefficient

CHCs were analyzed based on previous methods (Mangayayam et al., 2018) using gas chromatography mass spectrometry (GC-MS) equipped with an automated headspace sampler (details in the Supporting Information, text S1). The concentration of CHCs sorbed by organo-HT was determined by subtracting the equilibrium concentration in the experiments from the one in the control. This is done to account for potential septum sorption, volatilization loses, or experimental errors. The amount of CHC sorbed (q_e) (mg of sorbate/g of sorbent) was determined by the following equation:

$$qe = \frac{(C0 - Ce).\,V}{m}, \quad (1)$$

where C_0 and C_e (mg/L) are initial and equilibrium concentrations

Table 1
Description of sorption experiments performed in this study.

Organo-HT type	Organo-HT treatment	Tested CHC	Tested CHC concentrations (mg/L)	pH	Water Matrix	Results section
Single sorbate system						
Mg_3Al-1-DF	Oven dried	PCE or TCE	0–40	9–9.5	MilliQ	3.2.1
Mg_3Al-DS	Oven dried	PCE or TCE	0–40	9–9.5	MilliQ	3.2.1
Mg_3Al-DS	Oven, freeze dried, not dried	TCE	0–35	9–9.5	MilliQ	3.2.1
Mg_3Al-DS	Not dried	PCE, TCE, 1,1,2-TCA, TCM or CT	0–400	9–9.5	MilliQ	3.2.2
Ternary sorbate system						
Mg_3Al-DS	Not dried	TCE, TCM, and 1,1,2-TCA	0–150	9–9.5	MilliQ, SGW or NGW	3.3
Mg_3Al-DS	Not dried	TCE, TCM, and 1,1,2-TCA	50	-	Varying pH in MilliQ	3.3
Multiple sorbate system						
Mg_3Al-DS	Not dried	Multiple CHCs	-	8–9.5	CGW	3.4

PCE: tetrachloroethylene; TCE: trichloroethylene; 1,1,2-TCA: 1,1,2-trichloroethane; TCM: trichlomethane; CHCs: chlorinated hydrocarbons; SGW: synthetic groundwater; NGW: Pristine natural groundwater; CGW: contaminated groundwater.

of CHC in solution, V (L) is the solution volume, and m (g) is the added sorbent mass. Sorption isotherms were obtained by plotting q_e versus C_e (amount sorbed vs equilibrium concentration). The sorption coefficient (K_d) for each sorbate was determined from a linear regression fit rationing q_e (mg/g) to C_e. Linear partition coefficients have been shown to depend on the organic content of the sorbent (Chiou, 2002). We tested for this here and normalized K_d values to the percentage of organic content OC (%) in the organo-HT (estimated from TGA data) and calculated the organic-matter-normalized partition coefficient (K_{om}):

$$K_{om} = K_d \text{ x } [100 \text{ x } f/OC\ (\%)], \quad (2)$$

where *f* corresponds to the fraction of carbon in the surfactant, i.e., weight of carbon in the surfactant divided by the surfactant molecular weight (Jobbágy and Regazzoni, 2006).

3. Results and discussion

3.1. Physico-chemical properties of organo-HT

PXRD patterns showed the characteristic basal spacing (d_{003}) of 7.7 Å for $Mg_3Al{-}CO_3$, (Miyata, 1983; Rives, 2001), while for organo-HT intercalated with DS and 1-DF, the $d_{(003)}$ increased to 26.4 Å and 23.9 Å, respectively, in agreement with previous studies (Clearfield et al., 1991; Wang et al., 2005; Bruna et al., 2006) (Figure SM-2). Considering a thickness of 4.8 Å for the brucite-like sheets (Miyata, 1975), the interlamellar distances for Mg_3Al-DS and Mg_3Al-1-DF were 21.6 Å and 19.1 Å, respectively; values very close to the chain lengths of these surfactants (Table SM-1). This suggested a monolayer vertical arrangement for the DS molecules and a slightly tilted arrangement for 1-DF molecules in the interlayer (Clearfield et al., 1991). The presence of the $d_{(110)}$ diffraction peak at 1.53 Å, corresponding to one half of dimension *a* (Rives, 2001), confirmed the successful synthesis of a HT phase. Similarly, FT-IR spectra of Mg_3Al-DS and Mg_3Al-1-DF showed characteristic absorption bands of a HT compound with strong bands at 500-800 cm^{-1} for metal-oxide-metal stretching modes (Figure SM-3). Intercalation of surfactants was confirmed by the absorption bands at 1220, 1186, 1064, and 1050 cm^{-1}, which are characteristic modes of S=O antisymmetric and symmetric stretching, C–H stretching (ca. 3000 cm^{-1}), and C–H bending (1469 cm^{-1}) (Wang et al., 2005; Bruna et al., 2006; Zaghouane-Boudiaf et al., 2011) (Table SM-3). PXRD and FT-IR results were further corroborated by chemical analyses of acid digested samples, which showed Mg/Al and Al/S ratios close to 3:1 and 1:1, respectively (Table SM-4). The organic content, OC (%) of the organo-HT was derived from chemical analyses (Table SM-4). This yielded an approximate OC content of 28.4% for Mg_3Al-DS and 31.4% for Mg_3Al-1-DF (Table SM-5). In comparison to the theoretical OC content (as calculated from their respective formula, Table SM-4), the OC content in Mg_3Al-DS and Mg_3Al-1-DF was slightly higher, by ~1% and 7%, respectively. This suggested that some surfactants also adsorbed to the HT surface, rather than intercalated, which has also been observed in previous studies (You et al., 2002b; Narine and Guy, 1981). These results could explain why some sodium was detected in the Mg_3Al-1-DF solids (Table SM-4), where some of the surfactant adsorbed to the surface charge compensation (Clearfield et al., 1991). The OC and water contents were further confirmed by TGA analyses (details in the Supporting Information, Figure SM-4 and Table SM-5).

In terms of organo-HT particle size and morphology, SEM and TEM images showed large particle aggregates with sizes between 40 and 200 μm (Figure SM-5a), while individual organo-HT platelets were nanometer sized (50–200 nm) with poorly defined edges (Figure SM-5b). The average cluster size, as determined by laser diffraction, was ~150 μm. The specific surface area (S_{BET}) of Mg_3Al-DS and Mg_3Al-1-DF were 0.9 and 0.4 m^2/g, respectively, which agrees with previous studies (You et al., 2002b; Bruna et al., 2006). The surfactant intercalation drastically reduced the specific surface area compared to the inorganic HT (45 m^2/g for $Mg_3Al{-}CO_3$ synthesized here) (Figure SM-6), which is interpreted to be caused by the strong aggregation of these particles (Figure SM-5a), likely further facilitated by the surface adsorbed surfactants. Other studies also reported on the strong aggregation of Mg_3Al-DS (Clearfield et al., 1991; You et al., 2002a) and Mg_3Al-1-DF (Wang et al., 2005) and the respective reduction in the specific surface area.

Overall, these characterization results showed that both organo-HT were successfully synthesized, with properties similar to previous studies (Clearfield et al., 1991; Wang et al., 2005; You et al., 2002a). Looking in more detail at the specific characteristics of these compounds, it seems that Mg_3Al-DS could be more suitable for CHC sorption as DS intercalation seems more effective compared to DF intercalation (i.e., less surface adsorbed). In terms of costs, Mg_3Al-DS would also be the preferred choice, as it is the cheaper compound to produce. Another observation that could be key for CHC sorption is that these organo-HT compounds aggregate very strongly, particularly during intermediate steps, i.e. drying (Figure SM-7), which potentially affects their sorption capacity. Based on these considerations, we therefore set up some initial sorption experiments to determine the most effective organo-HT and post-synthesis treatment.

3.2. Sorption experiment in single solute systems

3.2.1. Effect of organo-HT properties on sorption yield

First, we tested whether CHC sorption by organo-HT is affected by the intercalated surfactant type (i.e., DS vs DF-1). Looking at the sorption isotherms for Mg_3Al-DS and Mg_3Al-1-DF (both dried the same way) in experiments with either PCE or TCE (Fig. 1a and Table SM-6), there were no significant differences in log K_{om} values (log $K_{om\ PCE} = 3.03{-}3.03$ and log $K_{om\ TCE} = 2.56{-}2.50$ for Mg_3Al-DS-Mg_3Al-1-DF, respectively). Similar log K_{om} values were reported for PCE (3.23) and TCE (2.60) sorption by oven dried Mg_3Al-DS synthesized the same way as in this study (Zhao and Nagy, 2004). To the best of our knowledge, there is no data on CHC log K_{om} values for Mg_3Al-1DF to compare with. Moreover, considering that Mg_3Al-1-DF surfaces were likely covered with excess surfactant (more so than for Mg_3Al-DS), this did not seem to affect the observed sorption properties. Overall, these results suggest that changing the functional group of the intercalated surfactant did not majorly impact sorption affinity towards these CHCs.

Next, we tested the effect of post-synthesis drying on organo-HT sorption capacity, shown in Fig. 1b. Slight differences were seen in the slope of the sorption isotherms, obtained for TCE by the two differently dried Mg_3Al-DS and the untreated Mg_3Al-DS (i.e., not dried, Fig. 1b). Specifically, log K_{om} was highest for untreated Mg_3Al-DS (log $K_{om\ TCE} = 2.71$), while drying seemed to decrease Mg_3Al-DS sorption capacity (i.e., log K_{om}), particularly when the organo-HT was freeze dried (log $K_{om\ TCE} = 2.37$) (Table SM-7). The lower log K_{om} values for dried Mg_3Al-DS are best explained by the lower reactive surface area. This is because drying induces the formation of larger aggregates that during re-suspension in water are not easily broken up (also visible in settling experiments, Fig. SM-7), due to the hydrophobic effect.

Based on these initial results, sorption efficiency of organo-HT toward CHC was clearly lower following post-synthesis drying, but less affected by surfactant type. However, seeing that Mg_3Al-DS synthesis is easier and more economical compared to Mg_3Al-1-DF (i.e. room-temperature synthesis, cheaper surfactant), Mg_3Al-DS

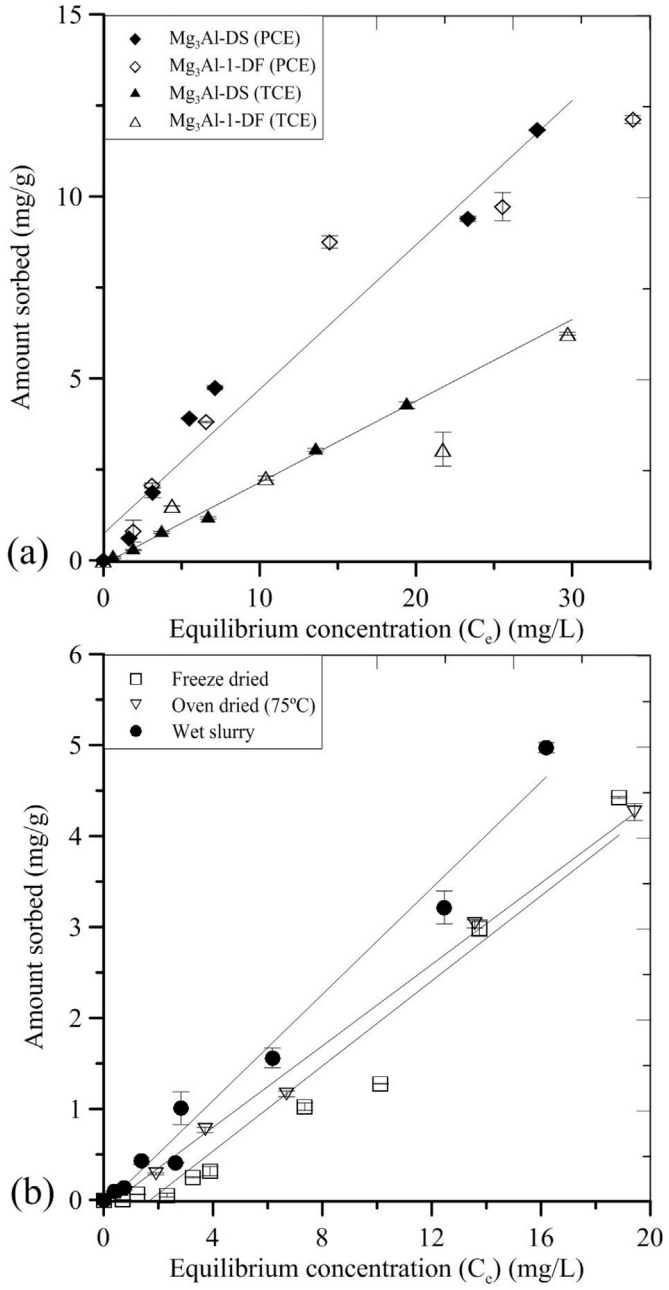

Fig. 1. (a) Sorption isotherms for (a) tetrachloroethylene (PCE) and trichloroethylene (TCE) by Mg_3Al-DS (◆, ◊) and Mg_3Al-1-DF (▲, Δ) as a function of intercalated surfactant anion, (equilibration time: 24 h; pH = 9–9.5; C_i = 0–40 mg/L). (b) Sorption isotherms for trichloroethylene (TCE) by Mg_3Al-DS as a function of various drying processes (Table SM-7) (equilibration time: 24 h; pH = 9–9.5; C_i = 0–35 mg/L). Data points represent the average of duplicate experiments.

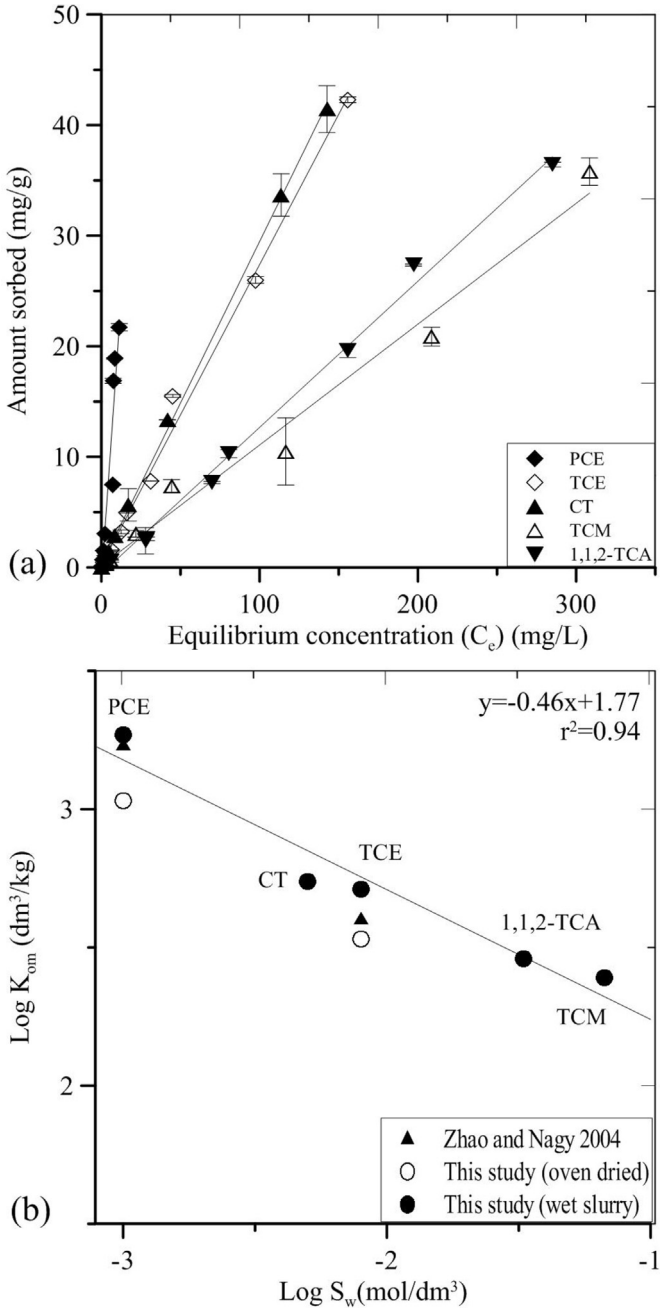

Fig. 2. (a) Sorption isotherms for a set of chlorinated hydrocarbons in single solute systems by Mg_3Al-DS (added as wet paste; equilibration time 24 h; pH = 9–9.5). Data points represent the average of duplicate experiments. (b) Log organic-matter-normalized partition coefficients (log K_{om}) (dm^3/kg) as a function of water solubility, i.e., hydrophobicity, of organic compounds at 25 °C (log S_w (mol/dm^3). For comparison, log K_{om} values reported by Zhao and Nagy (2004) for PCE and TCE sorption by dried Mg_3Al-DS are also shown. PCE: tetrachloroethylene, TCE: trichloroethylene, VC: Vinyl chloride, 1,1-DCE: 1,1 dichloroethylene, cis-DCE: cis-dichloroethylene, trans-DCE: trans-dichloroethylene, 1,1-DCA: 1,1 dichloroethane, 1,2-DCA: 1,2 dichloroethane, 1,1,2-TCA: 1,1,2-trichlorethane.

is clearly a more suitable sorbent. We therefore performed all further sorption experiments with non-dried Mg_3Al-DS.

3.2.2. Sorption behavior of single CHCs solute systems

The hydrophobicity (i.e., water solubility, S_W) amongst CHCs varies (Table SM-1), which ultimately controls the extent by which they can be sorbed by organo-HT (Jobbágy and Regazzoni, 2006). For the first time, we determined sorption isotherms for non-dried Mg_3Al-DS in single solute systems with PCE, TCE, CT, TCM, and 1,1,2-TCA shown in Fig. 2a (log K_{om} given in Table SM-8). For the CHC types and concentration range (C_0 = 0–400 mg/L) studied here, the sorption isotherms were linear and log K_{om} values were clearly highest for PCE and lowest for TCM. Plotting the derived log K_{om} values against the respective CHC hydrophobicity showed an inverse linear relationship (Fig. 2b), similar to what was observed for aromatic compounds (Jobbágy and Regazzoni, 2006). The previously reported log K_{om} for PCE and TCE sorption by dried Mg_3Al-DS also agree well with these trends (Zhao and Nagy, 2004, Fig. 2b),

although those were determined for a much lower concentration range (0–35 mg/L). The fact that the isotherm was linear over the entire tested CHC concentration range indicates that CHC sorption is controlled by partitioning into the organic interlayer (i.e. organic content OC (%)) rather than by physical adsorption (Chiou et al., 1979; Chiou, 2002). Similar linear isotherms were also described for sorption of hydrophobic chemicals into organic matter and soils (Delle Site, 2001; Karickhoff et al., 1979).

3.3. Sorption experiment in a ternary solute system

To understand more complex, "real-life" systems, we examined the sorption capacity of Mg_3Al-DS in ternary solute systems (TCE, TCM, and 1,1,2-TCA) testing 3 different water chemistry (MilliQ, SGW, and NGW) and varying pH (6-11). TCE, TCM, and 1,1,2-TCA were selected because each represents one of the most common CHCs families (methanes, ethanes, and ethenes) and they share the same number of chlorine atoms.

3.3.1. Effect of water chemistry

All sorption isotherms were linear over the tested CHC concentration range (MilliQ, SGW, and NGW; Fig. 3) and log K_{om} values were similar amongst the three tested waters (Table SM-9). Identical to the single solute system, log K_{om} values correlated linearly with CHC hydrophobicity (TCE>1,1,2-TCA > TCM). Note however, that absolute log K_{om} values in ternary solute systems were generally 4–9% lower (Table SM-9) compared to log K_{om} values in single solute systems (Table SM-8), thus giving a slightly modified linear relationship between log K_{om} and log S_w (section 3.4). Overall, these results re-affirmed observations in single solute systems and earlier studies (Jobbágy and Regazzoni, 2006) that solute partitioning is the main mechanism of CHC sorption by Mg_3Al-DS, even if the water matrix is more complex. In addition, we show that sorption does not majorly depend on the co-existence of multiple CHCs (Fig. 3), i.e., that the affinity of Mg_3Al-DS towards a specific CHC compound is mainly governed by the CHC hydrophobicity, i.e., water solubility. This also fits with previous work on CHC sorption by soils (Chiou et al., 1983), where it is argued that there is little competitive sorption between the different nonionic organic compounds.

3.3.2. Effect of pH

Seeing little difference in log K_{om} values between the different waters, the effect of pH on Mg_3Al-DS sorption capacity was only investigated for the MilliQ ternary system. The pH range (6–11) was chosen based on the stability range reported for Mg_3Al–Cl HT (Jobbágy and Regazzoni, 2011) and the pH expected for natural groundwater (pH 6.5–8; Custodio and Llamas, 1996). Overall, no significant change in CHC uptake was observed with a change in pH (Fig. 4) demonstrating the Mg_3Al-DS compound was stable and kept its sorption capacity over a wide pH range. While no other study has examined pH effects in ternary solute systems, similar insignificant pH effects were also shown for the sorption of acid dye by Mg_2Al-DS (pH 5–9) (Bouraada et al., 2009) and sorption of anionic dye by Mg_2Al–CO_3 (Zhu et al., 2005).

3.4. Sorption experiments with contaminated groundwater

Contaminated groundwater is often far more complex than our ideal laboratory systems, and will include contaminants and

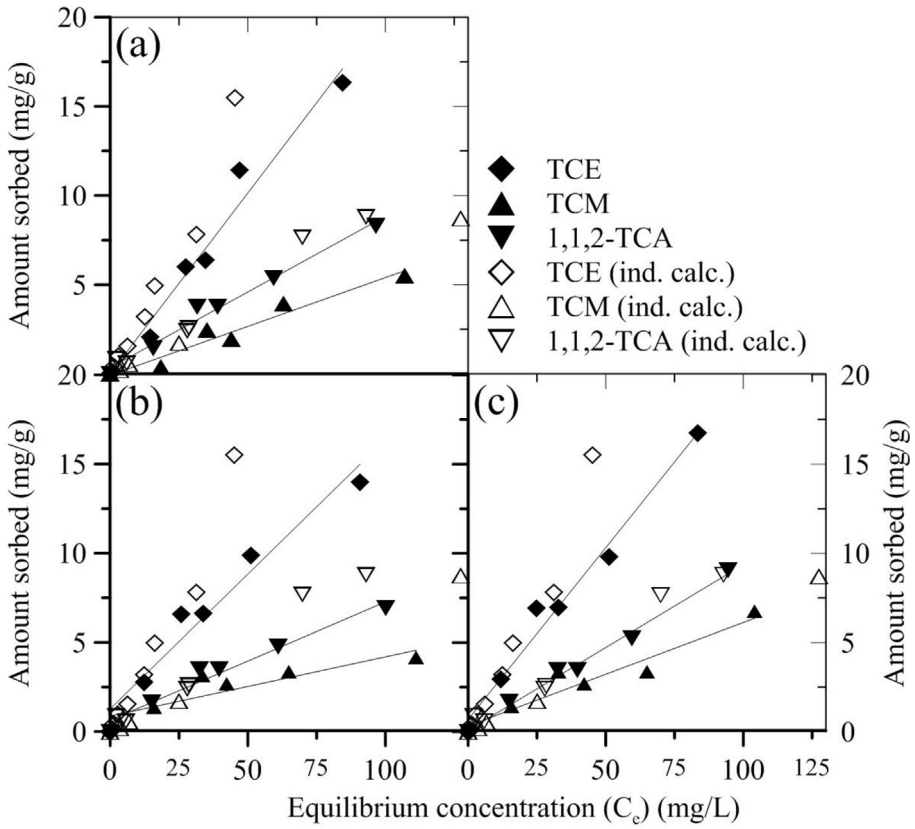

Fig. 3. Sorption isotherms from ternary solute systems (TCE, TCM, and 1,1,2-TCA) for Mg_3Al-DS in (a) MilliQ, (b) natural groundwater, and (c) synthetic groundwater (filled symbols). Lines represent the best fit to the linear regression curves with r^2 values greater than 0.90. Data points represent the average of duplicate experiments. For comparison, sorption data from single solute systems (Fig. 2a) are also shown (unfilled symbols).

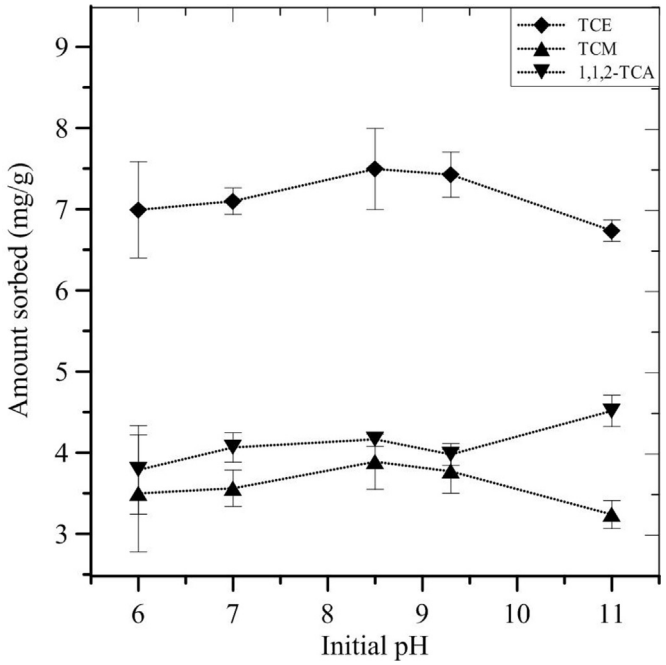

Fig. 4. Effect of pH on the sorption of CHC in a ternary system (TCE, TCM, and 1,1,2-TCA) by Mg_3Al-DS in MilliQ. ($C_0 = 50$ mg/L). (◆) trichloroethylene (TCE), (▲) trichloromethane (TCM), and (▼) 1,1,2-trichloroethane (1,1,2-TCA). Data points represent the average of duplicate experiments.

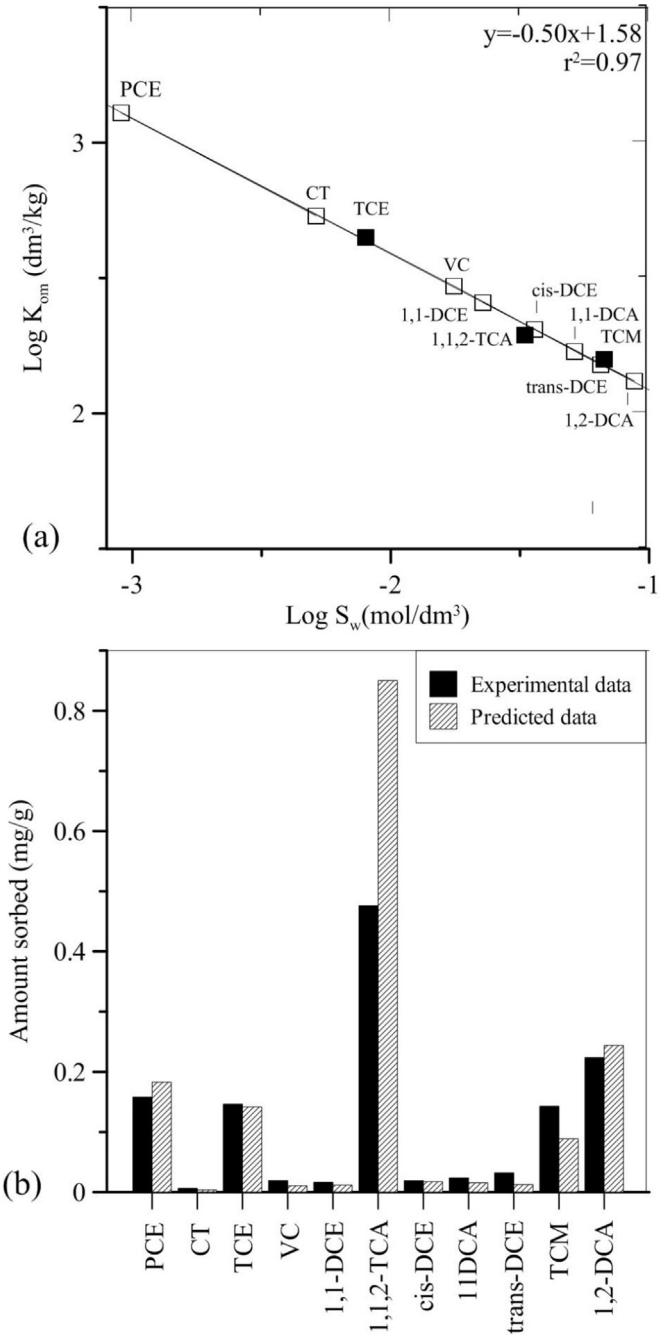

Fig. 5. (a) Organic-matter-normalized partition coefficients (log K_{om}) (dm^3/kg) as a function of water solubility of organic compounds at 25 °C (log S_w (mol/dm^3). Data calculated from sorption isotherms from ternary solute system in NGW (unfilled symbols). Data predicted from log K_{om} = -0.50*log (S_w)+1.58 ($r^2 = 0.97$) (Filled symbols). (b) Predicted amount sorbed (mg/g) (as derived from Fig. 5a) vs experimental amount sorbed (mg/g) calculated from sorption experiments with contaminated groundwater. PCE: tetrachloroethylene, TCE: trichloroethylene, VC: Vinyl chloride, 1,1-DCE: 1,1 dichloroethylene, cis-DCE: cis-dichloroethylene, trans-DCE: trans-dichloroethylene, 1,1-DCA: 1,1 dichloroethane, 1,2-DCA: 1,2 dichloroethane, 1,1,2-TCA: 1,1,2-trichlorethane. (b) Comparison between predicted and experimental amount of individual CHCs sorbed by Mg_3Al-DS in NGW.

conditions that have not been and/or could not be tested in the laboratory. Therefore, it is important to assess the validity of observed relationships, i.e., models, to predict the behavior of newly developed reactants in "real-life" systems before their application at a larger scale. Here we used the observed linear relationship between log K_{om} and log S_w from the ternary CHCs systems in NGW (log $K_{om} = -0.50$*log S_w+1.58, $r^2 = 0.97$; Fig. 5a) to predict log K_{om} values for CHCs, whose log K_{om} values were not determined under laboratory conditions (Table SM-10). Based on these log K_{om}, we then determined the amount of CHCs that should theoretically be removed by Mg_3Al-DS and compared these values to actual CHCs sorption yields measured in the collected contaminated groundwater (Fig. 5b, Table SM-10). Overall, there is fairly good agreement between predicted and measured values. Two clear outliers are: 1,1,2-TCA, where the sorption yield was ~44% lower than the predicted value; and TCM, where the yield was ~38% higher than the predicted value. The possibility that the groundwater chemistry impacted these results cannot be excluded and should be investigated further. Overall, our results indicate that the applied linear log K_{om}-log S_w relationship can predict log K_{om} for many CHC, but may work less well for others (e.g., TCM, 1,2-TCA) in complex, real groundwater systems.

4. Benefits of using organo-HT for decreasing CHCs concentration in contaminated groundwater

Activated carbon (AC) is one of the most widely-used sorbent for removal of CHCs from waste streams (Pavoni et al., 2006). The sorption of CHCs onto AC is characterized by a strong solute uptake but non-linear isotherms, which resulted in the ultimate saturation of the sorbent (Smith et al., 1990). Additionally, AC performance is affected by the presence of multiple CHCs (as expected in contaminated groundwater). For example, it has been shown that in binary solute systems there is a clear competition between CHCs for adsorption on AC (Bansal and Goyal, 2005). The same sorption mechanism was reported for nonionic organic compounds into cationic clays (Smith and Galan, 1995). Organo-clays are similarly effective at sorbing CHC sorbents (compared to the organo-HTs tested in this study and elsewhere (Zhao and Nagy, 2004)), and have been proposed for use as a pre-treatment filter material to

remove competitive compounds (e.g., aromatic hydrocarbons such as toluene, Alther (2002)) to optimize AC sorption capacity. Based on observations in this study, organo-HT could be used in a similar way (as pre-filters) to optimize the lifetime of fix-bed AC filters and efficiently decrease the concentration of CHCs from aqueous media. These observations include: (a) that the linear relationship between sorption efficiency and the hydrophobicity of the CHC is independent of the size of the CHC molecules, (b) CHC sorption occurs by solute partitioning, i.e., no saturation observed at high concentrations (>400 mg/L), (c) little sorption competition between CHCs in mixtures, (d) easy and low cost Mg_3Al-DS synthesis.

It is important to consider that this study determined CHC sorption uptake by organo-HT in different water chemistry, at varying pH, and in the presence of multiple CHCs. However, other variables such as the long-term fate and stability of organo-HT under laboratory and field conditions should be studied next to further evaluate their suitability for remediation applications.

5. Conclusions

The conclusions drawn from the current study are summarized as follows:

- The intercalation of DS and 1-DF in Mg/Al HT produces hydrophobic nanoparticles that enhance the amount of CHC sorbed in single solute systems. All sorption isotherms were linear and yielded log K_{om} values that correlate inversely with CHCs hydrophobicity (S_w). The linearity of the sorption isotherm demonstrated that the main mechanism of sorption is solute partitioning. In this study, we further showed that this inverse relationship between log K_{om} and S_w is also valid in waters where multiple CHCs are present, confirming that there is little competition between CHCs for sorption by organo-HT.
- Mg_3Al-DS can be applied as wet paste or as dried nanomaterials depending on the chosen application (e.g. filters, permeable reactive barriers), creating a variety of options for their potential use in groundwater remediation. However, these materials strongly aggregate with drying, decreasing the number of active sorption site. Thus, this aspect and potential modifications to create more porous aggregates should be investigated in future studies.
- Individually calculated K_{om} values for Mg_3Al-DS and their correlation with S_w were used predict unknown K_{om} in complex contaminated groundwaters. However, it is recommended to carry out specific sorption experiments with selected contaminated groundwater and the present CHCs.

Acknowledgments

The authors thank Alexander Misol and Raquel Trujillano for their help with organo-HT synthesis, Clara Ribargorda, Amaya Sayas and Irene Esteban for their help in the field, Denis Okhrimenko for BET measurements and Jeffrey P. Perez for TEM data collection and analysis. This study was funded by Metal-Aid Innovative Training Network (ITN), supported by a grant from the European Commission's Marie Skłowdowska Curie Actions program (No 675219).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2019.124369.

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